THESIS

EXPERIMENTAL STUDY OF A NOVEL SYNTHESIS STRATEGY OF CORE-SHELL STRUCTURED MICRO-PARTICLES VIA CYCLIC GAS-SOLID REACTIONS

Submitted to

The Engineering Honors Committee

119 Hitchcock Hall

College of Engineering

The Ohio State University

Columbus, Ohio 43210

By

Zhenyang Wang

William G. Lowrie Department of Chemical and Biomolecular Engineering

140 West 19th Ave, Columbus, Ohio.

February 20, 2014

Abstract

At present, coating and coating-like process act as common methods of synthesizing particles, which usually have high utility consumption thus have high cost. Besides, the waste solution from the coating or coating-like processes needs further treatment to avoid hazards emission to the environment. In this study, a novel strategy is introduced to the synthesis of core-shell particles. The new strategy employs the irreversible solid-gas reaction cycle (eg,. Reduction and oxidation of metal), inducing a solid-phase ionic diffusion of effective material to the surface of the particles gradually. Different form the coating process. This novel strategy only involves the gas-solid reaction. Thus it avoid the treatment of waste solution and is thought to be more environmental-friendly. In addition, this synthesis method does not require specified coating but use the normal gas-solid reactor. So the cost can be lower than the conventional methods. To further illustrate this new strategy, micrometer- sized particles which contain the mixture of Fe_2O_3 and Al_2O_3 powders are used. This kind of particles is conducted H_2 reduction and O_2 oxidation reactions for certain number of cycles at high temperature. The ionic diffusion of Fe cations is known to take place during the reaction cycles. Through SEM and EDX analysis, the formation of core-shell structure is verified. The particles maintain an Al_2O_3 core-Fe_2O_3 shell structure. A comparative study is conducted using Fe_2O_3 and TiO_2. For particles with the cyclic reaction through the diffusion of gaseous O anions, SEM and EDX analysis fail to verify the formation of desired structure. The two sample researches indicate that solid phase ionic diffusion’s dominating role in the formation of core-shell structure. Besides the comparative research, a 2-D diffusion model is employed to simulate this novel strategy.

Contents

Introduction

The term “core-shell” first began in the research of semiconductors in the late 1980s and early 1990s.[1-3] This structure has gained its popularity in the past decades due to its advanced physical, chemical and mechanical properties. With the larger implication of core-shell structure particles in modern chemical and pharmaceutical industry, the research of formation and application for core-shell particles remain a hot topic in academia.

Core-shell particles have numerous advantages in catalytic process. Generally particles in core-shell structure can be divided into two categories: One with effective material forming the core and the other has the effective material mainly distributed in the shell. For the former one, the shell with ineffective material can control the reaction rate by affecting the diffusion rate of reactants into the particles. The shell can also act as a protective layer preventing the core material from high temperature, side-reactant or others that will result in the decay of the effective material. Furthermore, in pharmaceutical industry, manufacturer can actually use the shell to maintain control of the releasing rate or releasing time for the core material for precise medical care.

For particles which have the effective material distributed in the shell, the core-shell structure can maintain the maximum surface area. The involvement of ineffective material as core can lower the consumption of effective material in each particle. Besides, with all the effective material in the shell covering the core, the diffusion resistant is much lower than the particle totally made of effective material.

Current method of synthesis for the core-shell particles includes coating, coating-like process-vapor deposition, mechanical granulation, solvent precipitation, sol-gel and hydrolysis.[4-18] However, it is not applicable for them to achieve both low cost and precise shell thickness control. The novel synthesis method that is discussed in this article, for certain properties of materials, this method can achieve desired low cost and thickness control. Using the cyclic gas-solid reactions, the shell material is gradually diffused from the mixture to form the shell. This diffusion can happen only if the shell material is a primary diffusing species in the reaction.[4-19]

In this study, a Fe_2O_3-Al_2O_3 powder mixture is used to form a Fe_2O_3-shell, Al_2O_3 core structure. The cyclic reaction is reduction with H_2 and oxidation with O_2. A comparative experiment is conducted with a Fe_2O_3-TiO_2 powder mixture to illustrate the dominant role of ionic diffusion in the formation of the core-shell structure. With the same cyclic reactions the second sample is not proposed to form the core-shell structure since its opposite mechanism form the first sample, which will be discussed in detail in the following section.

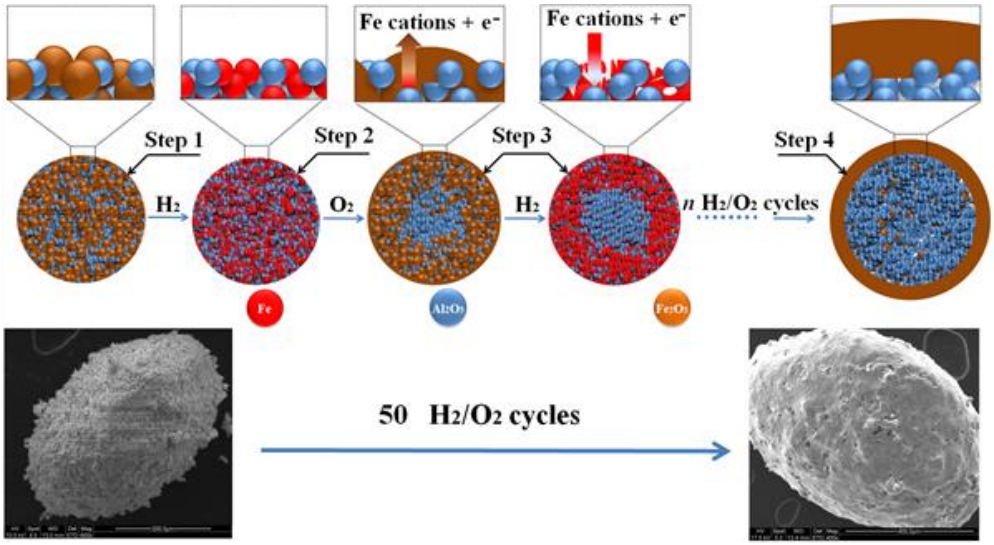

Figure 1: Preparation procedure of desired Al_2O_3core - Fe_2O_3shell structure

Theory and Strategies

During the formation of the core-shell particles, only the shell material reacts with gaseous reactants. Figure 1 shows the proposed steps that the mixture of Fe_2O_3 and Al_2O_3 forms core-shell structure.

Step 1: For a general process, the shell material "A" (Fe_2O_3 in this study) is mixed homogeneously with the core material "B" (Al_2O_3 in this study). The mixture is made into certain size (1-2 mm in this study). It is noted that either the shell material "A" or the corresponding material reacted with gaseous reactants "C" can be used to make the mixture and undergo the cyclic reactions.

Step 2: A pair of cyclic gaseous reactions are chosen. Shell material A reacts with gaseous reactant 1 to gain C and gaseous product. For the reversible reaction, C is reacting with gas reactant 2 to get A as well as another gaseous product. In this study, the reversible reactions used are listed below:

$Fe_2O_3(s) + H_2(g) \rightarrow 2Fe(s) + 3H_2O(g)$ (1)

$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$ (2)

For the reversible reactions pair that is chosen, one is supposed to be volume increasing reaction and the other should be volume decreasing. In this study, when the Fe_2O_3 is reduced by H_2, there is volume decreasing happening inside each particle, causing the formation of cracks and pores, which allow H_2 react with Fe_2O_3 inside the particles.

Step 3: During the process of reaction 2, O_2 will first oxidize the outer layer Fe, which causes the volume increasing. The expanding surface layer with dense structure Fe_2O_3 will prevent the diffusion of oxygen into the inner particle. Without direct contact with oxygen, Fe cations interior the particle will conduct an outward diffusion with the Fe cations concentration gradient being the driving force. Previous researches and studies focus on this kind of ionic diffusion in a grain level. However, the gas-solid ionic diffusion can actually take place in a larger scale.[20,21] Due to the extent of reaction in the reduction/oxidation cycles, not all the

voids are blocked thus there is still inward O_2 diffusion taking place. As a result, only a small portion of Fe cations will diffuse outward per reaction cycle.

The choice of core and shell materials is of great significance to the formation of desired structure. The core-shell structure can only form when the shell material is the solid-phase ionic diffusion species. If the reversible reactions mainly depend on the inward and outward diffusion of gaseous reactant, (oxygen) the shell species will just increase/decrease its volume at its original location without relatively long distance migration. Besides, the core material that is chosen is not supposed to participate in the solid-phase ionic diffusion or react with the gaseous reactant to ensure the migration of shell material.

After a single step of shell material outward diffusion is completed, the reverse reaction will induce a backward diffusion of shell material. The Fe cations are supposed to diffuse back to its original location if the reaction is perfect reversible. However, pores will be formed when the reversible reactions take place because of the volume decreasing reaction (reduction), which prevents the backward diffusion of shell species. H_2 goes into the cracks and react with Fe_2O_3 before they diffuse backward. So each pair of reversible reactions will induce a certain amount of shell material to diffuse outward and remain on the surface of the particle.

Step 4: After n cycles of reversible reactions, most of the shell material have gradually migrated to the surface and form the shell while the inert of the particles contain mainly core material. Thus the core-shell structure is formed. The formation of this structure has direct connection with the reversible reactions types and number of cycles. Micro-size particles with smaller diameter would require less reaction time and less cycle of reversible reactions. Also particles with shell species having higher diffusivity would reach core-shell structure more quickly.

Experiments

This study uses Fe_2O_3 (<3μm), TiO_2 (<3μm) and Al_2O_3 (<75μm) to compose particles in the same size. 25%H2 with 75% N2 is used for reduction reaction. 25% ambient air mixed with 75% N2 is used for oxygenation.
The particles that are used for experiment is made of 30 wt% Fe_2O_3 and 70 wt% Al_2O_3. The powders are well mixed in water and then dried to sieve particles in the size of 1mm or smaller. The particles are loaded to the thermogravimetric analysis (TGA) to conduct 50 reduction cycles and 50 oxidation cycles at 900 ºC. Each reaction takes 30 min including 5 min N2 flushing. For comparison, another particles made from a mixture of 30 wt% Fe_2O_3 and 70 wt% TiO_2 goes through the same reduction and oxidation cycles. The samples are loaded to Quanta 2000 SEM analyzer with some of the particles scratched and cracked by mechanical force to examine the interior structure.

Result and Analysis

Figure 2 shows the surface and its element analysis for unreacted particles of Al_2O_3-Fe_2O_3 mixture. From the figure it can be seen that surface is bumpy with pores and seams. The element analysis shows that there is coexistence of Al_2O_3 and Fe_2O_3on the surface, which agrees with the mixture property of the particles.
Figure 3 shows the EDX for the reacted particle and the particle which is peeled into half to see the interior structure. It can be obviously seen that the reacted particle is smooth on surface compared with the unreacted one. From the previous work, the outward ionic diffusion of solid reactant tends to smooth the surface area. Thus the smooth area of this particle can be one of the proofs of outward ionic diffusion.[22] The core part from the figure is porous due the fact of outward diffusion of Fe cations that is discussed in the theory section.

Figure 4 is the surface analysis for the reacted particle on smaller scope and corresponding element analysis. Several points are randomly picked to do the EDX element analysis, the element analysis only shows the signals of Fe and O without Al, which means that surface, is compromised by Fe_2O_3 mainly. This analysis agrees with the theory that Al_2O_3 not participating the outward ionic diffusion.
A reacted particle is peeled into half to exam the interior structure in SEM and EDX. In figure 5 an obvious shell structure can be observed. EDX analysis shows the core is comprised mainly by Al and O while a much weaker Fe signal is detected. When examining the edge of the particle, the approximate thickness of the shell is about 2-3μm. EDX analysis of the cross section again confirms that the shell is compromised by Fe and O, which should be Fe_2O_3 based on the theory. Since the shell is formed due to the Fe cations diffusion, the shell thickness can be monitored by controlling the concentration of Fe_2O_3 in the mixture.

The particles made of mixture of TiO_2 and Fe_2O_3 also go through the SEM and EDX analysis. However, this mixture does not apply this outward diffusion mode and form the core-shell structure. If Fe_2O_3 is mixed with TiO_2, O anion will become the main diffusion specie in the oxidation and reduction cycle. O anion will diffuse inward to react with Fe in the oxidation step, expanding the volume of the particles and it will diffuse outward in the reduction step. The reversible reactions for Fe_2O_3-TiO_2 mainly depend on the inward and outward diffusion of O anions. If the mechanism of ionic diffusion also applies for Fe_2O_3-TiO_2 particles, the Fe_2O_3 species in the particle, during the cyclic reactions, will locally expand and shrink without long migrating in a relatively long distance to form the shell structure. It can be observed from figure 7 that unreacted Fe_2O_3-TiO_2 has similar structure with unreacted Al_2O_3-Fe_2O_3 with pores and seams on the surface. Further element analysis show the coexistence of Fe and Ti signal, which agrees with the mixture property that forms the particles. The reacted Fe_2O_3-TiO_2 particle under SEM appears with more pores and seams which have larger void. From previous literature the reason for this is sintering.[22] The coexistence of Ti and Fe on the surface illustrate that no core-shell structure is formed during the cyclic reactions, which agree with the theory.

The reason for the mixture of Fe_2O_3 and TiO_2 not forming core-shell structure remains

unclear. From now the research group believes that is it because Fe_2O_3 and TiO_2 diffuse into each other, destroying the crystal structure and making numerous oxygen vacancies for O anion to pass through. The vacancies significantly increase the diffusion rate of O anion, making it much faster than Fe cations diffusing outward. Thus the O anions become the main diffusion species and the Fe cations will just expand and shrink locally without "long distance" migration and no core-shell structure is formed.[23]

The novel strategy that is discussed in this study has several advantages over the conventional methods. First of all, the new strategy only need normal high temperature reactor for production while some methods like vapor deposition need far more expensive facilities, which is a huge saving in capital cost. In addition, using solid-phase ionic diffusion avoids the use of solution which is commonly employed in coating or coating like processes, which often need to deal with the waste solution. And the only side product in this reversible reactions cycle is water, making the process more environmental friendly. Besides, the new strategy can have precise control in the thickness of the particle by changing the amount of desired shell species in material mixture. It is noted that reduction-oxidation reaction cycle is not the only reversible reactions that can be used in the production. Other reversible reactions are proposed to play the similar roles concerning the desired shell species.

However, the new strategy does have disadvantages. The high temperature reactor may require high energy input. Desired shell species and core species must match with proper reversible reactions. The formation of core-shell structure needs long reaction cycles thus long time period.

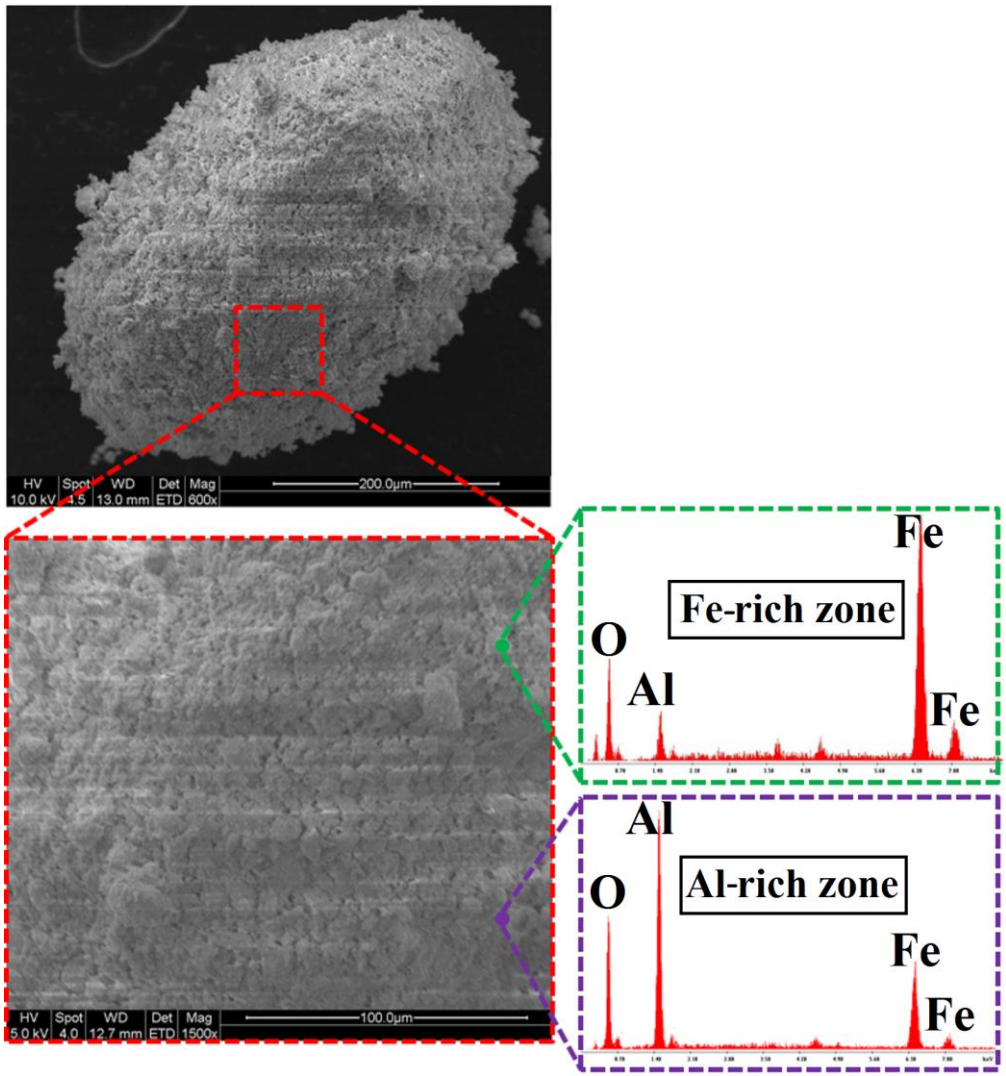

Figure 2: SEM and EDX for an unreacted Fe_2O_3-Al_2O_3 prticle.

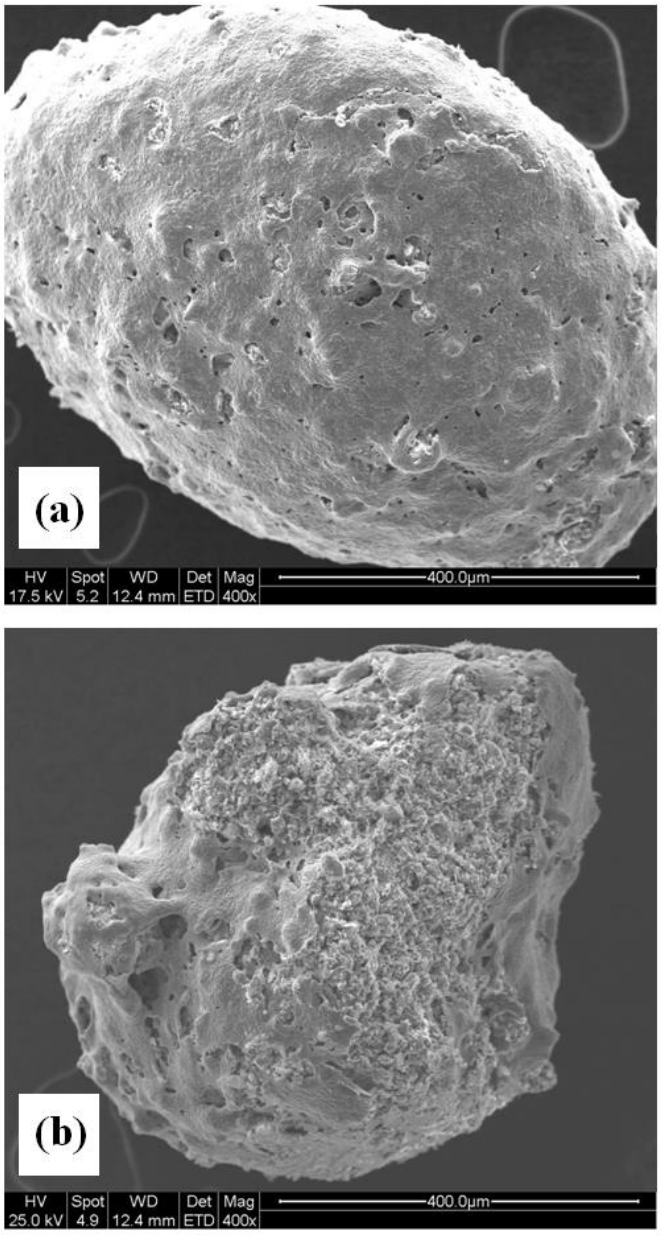

Figure 3 SEM figure for an intact (a) and peeled (b) Fe_2O_3-Al_2O_3 particle

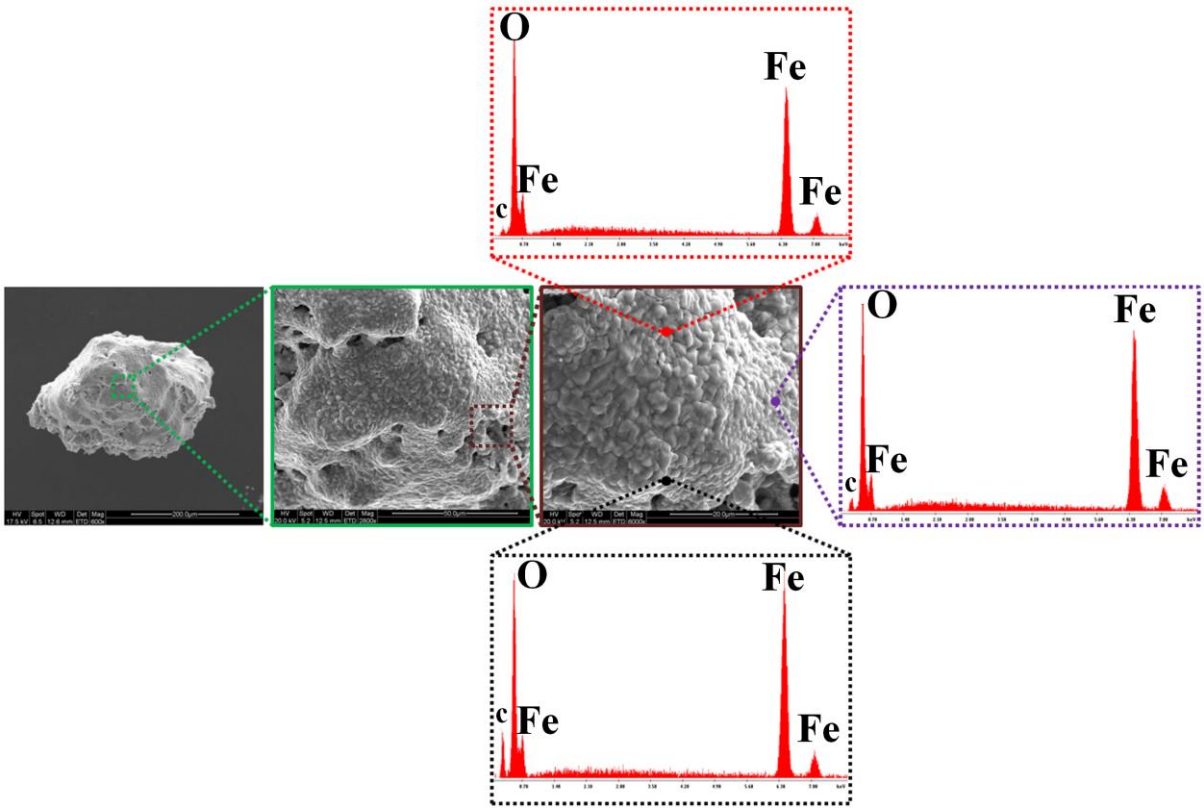

Figure 4: SEM in smaller scope with element analysis for the shell of a Fe_2O_3-Al_2O_3 particle.

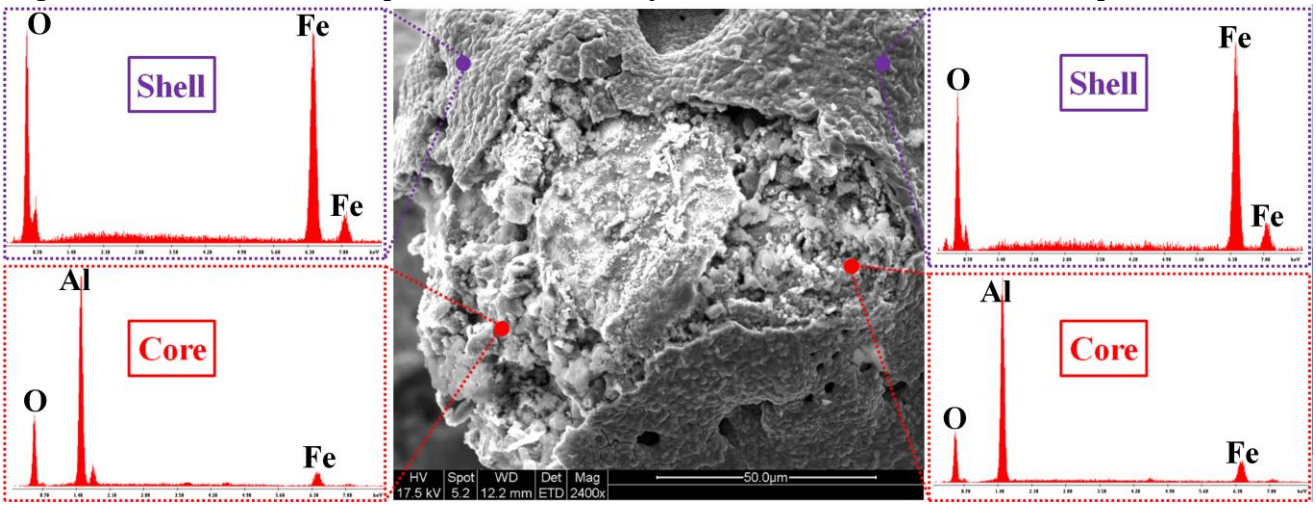

Figure 5: SEM and EDX for partially peeled Fe_2O_3-Al_2O_3 particle.

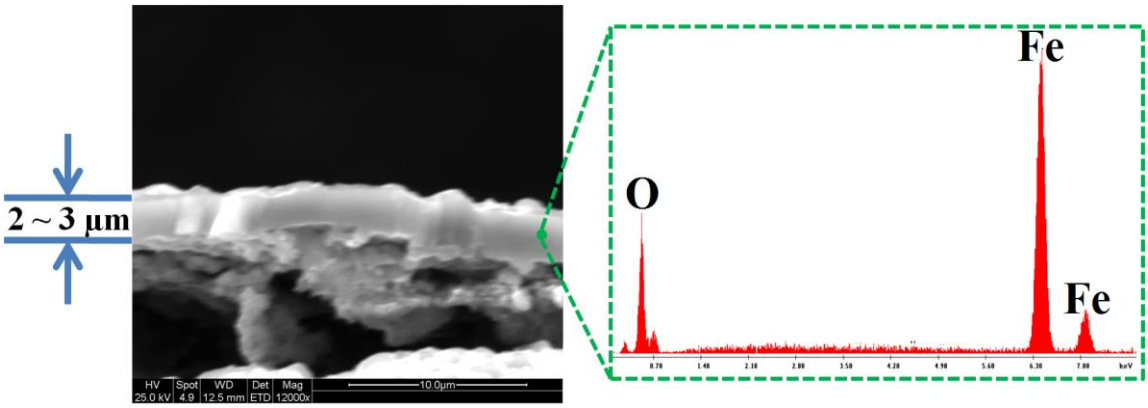

Figure 6: SEM and EDX for shell structure of a reacted Fe_2O_3-Al_2O_3 particle.

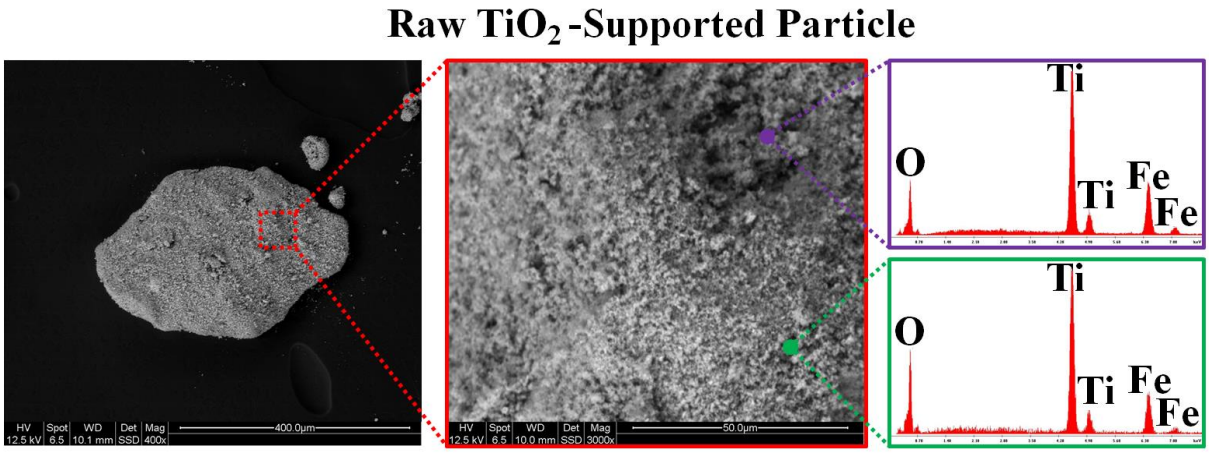

Figure 7: SEM and EDX for an unreacted Fe_2O_3-TiO_2 particle.

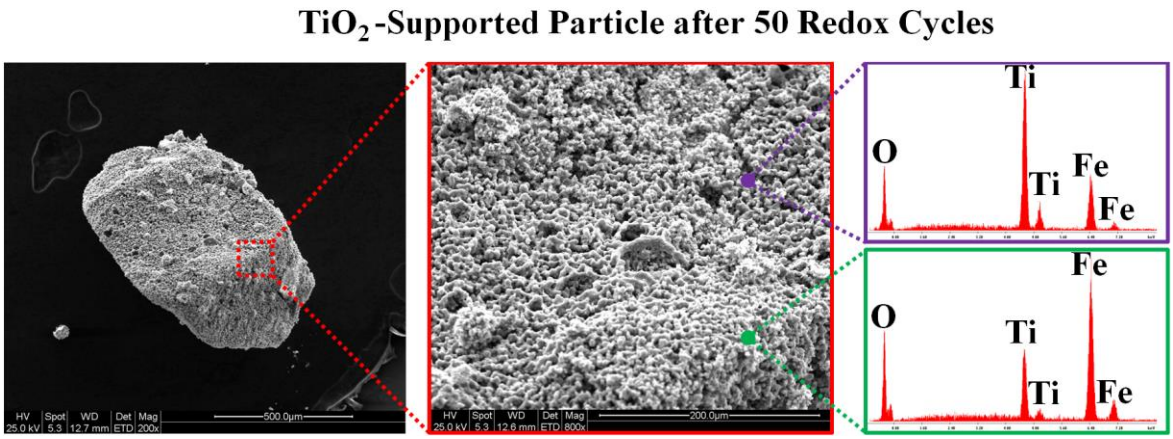

Figure 8: SEM and EDX for a reacted Fe_2O_3-TiO_2 particle.

Conclusions

In this study a new strategy of producing core-shell structure microparticles is explored. The experiment result shows that solid-phase ionic diffusion in reversible reaction cycle can form core-shell structure when the shell species is the mainly diffusion species. This study uses Fe_2O_3-TiO_2 mixture particles and Al_2O_3-Fe_2O_3 particles, trying to develop a general mechanism for the formation of core-shell structure. H_2 reduction and ambient air oxidation are chosen as the reversible reaction cycles. The Al_2O_3-Fe_2O_3 particles form desired structure after the cyclic reactions while Fe_2O_3-TiO_2 does not, which can be seen as a proof of the theory that is developed in this study. However, more experiments are necessary to generalize this new strategy before it can be applied to the industrial production. The new strategy has its unique advantages. Compared with conventional method, it is more environmental friendly, energy-saving and low cost. The application of this new strategy would be a new way for the manufacturers to consider producing the core-shell particles.

Reference

(1) Henglein, A. Small-Particle Research: Physicochemical Physicochemical Properties of Extremely Small Colloidal Metal and Semiconductor Particles. Chem. Rev. 1989, 89, 1861.
(2) Spanhel, L.; Weller, H.; Henglein, A. Photochemistry of Semiconductor Colloids. 22. Electron Injection from Illuminated CdS into Attached TiO2 and ZnO Particles. J. Am. Chem. Soc. 1987, 109, 6632.
(3) Youn, H.-C.; Baral, S.; Fendler, J. H. Dihexadecyl Phosphate, Vesicle-Stabilized and in Situ Generated Mixed Cadmium Sulfide and Zinc Sulfide Semiconductor Particles: Preparation and Utilization for Photosensitized Charge Separation and Hydrogen Generation. J. Phys. Chem. 1988, 92, 6320.
(4) Chaudhuri, R. G.; Paria, S. Core/Shell Nanoparticles: Classes, Properties, Synthesis Mechanisms, Characterization, and Applications. Chem. Rev. 2012, 112, 2373.
(5) Sarhar, Z.; Sun, Z.; Zhao, D.; Kaliaguine, S. Development of Sinter-Resistant Core−Shell LaMnxFe1−xO3@mSiO2 Oxygen Carriers for Chemical Looping Combustion. Energy Fuels 2012, 26, 3091.
(6) Park, J.-I.; Cheon, J. Synthesis of “Solid Solution” and “Core-Shell” Type Cobalt−Platinum Magnetic Nanoparticles via Transmetalation Reactions. J. Am. Chem. Soc. 2001, 123, 5743.
(7) Fan, J. A.; Wu, C. H.; Bao, K.; Bao, J. M.; Bardhan, R.; Halas, N. J.; Manoharan, V. N.; Nordlander, P.; Shvets, G.; Capasso, F. Self-Assembled Plasmonic Nanoparticle Clusters. Science 2010, 328, 1125.
(8) Fan, J. A.; Bao, K.; Sun, L.; Bao, J. M.; Manoharan, V. N.; Nordlander, P.; Capasso, F. Plasmonic Mode Engineering with Template Self-Assembled Nanoclusters. Nano Lett. 2012, 12, 5318.
(9) Fan, J. A.; He, Y.; Bao, K.; Wu, C. H.; Bao, J. M.; Schade, N. B.; Manoharan, V. N.; Shvets, G.; Nordlander, P.; Liu, D. R.; Capasso, F. DNA-Enabled Self-Assembly of Plasmonic Nanoclusters. Nano Lett. 2011, 11, 4859.
(10) Laurent, S.; Forge, D.; Port, M.; Roch, A.; Robic, C.; Elst, L. V.; Muller, R. N. Magnetic Iron Oxide Nanoparticles: Synthesis, Stabilization, Vectorization, Physicochemical Characterizations, and Biological Applications. Chem. Rev. 2008, 108, 2064.
(11) Yan, E.; Ding, Y.; Chen, C.; Li, R.; Hu, Y.; Jiang, X. Polymer/Silica Hybrid Hollow Nanospheres with pH-Sensitive Drug Release in Physiological and Intracellular Environments. Chem. Commun. 2009, 19, 2718.
(12) Ishizu, K.; Onen, A. Core-Shell Type Polymer Microspheres Prepared by Domain Fixing of Block Copolymer Films. J. Polym. Sci., Part A: Polym. Chem. 2003, 27, 3721.
(13) Caruso, F. Nanoengineering of Particle Surfaces. Adv. Mater. 2001, 13, 11.
(14) Phadtare, S.; Kumar, A.; Vinod, V. P.; Dash, C.; Palaskar, D. V.; Rao, M.; Shukla, P. G.; Sivaram, S.; Sastry, M. Direct Assembly of Gold Nanoparticle “Shells” on Polyurethane Microsphere “Cores” and Their Application as Enzyme Immobilization Templates. Chem. Mater. 2003, 15, 1944.
(15) Sgraja, M.; Bertling, J.; Kummel, R.; Jansens, P. J. Inorganic and Hybrid Hollow Spheres by Coating of Microcapsules as Templates. J. Mater. Sci. 2006, 41, 5490.
(16) Ma, J.; Sahai, Y. Effect of Electrode Fabrication Method and Substrate Material on

Performance of Alkaline Fuel Cells. Electrochem. Commun. 2013, 30, 63.
(17) Ma, J.; Sahai, Y. A Direct Borohydride Fuel Cell with Thin Film Anode and Polymer Hydrogel Membrane. ECS Electrochem. Lett. 2012,1, 41.
(18) Ma, J.; Sahai, Y. Cost-Effective Materials for Direct Borohydride Fuel Cells. ECS Trans. 2012, 42, 101.
(19) Wei, S.; Wang, Q.; Zhu, J.; Sun, L.; Lin, H.; Guo, Z. Multifunctional Composite Core−Shell Nanoparticles. Nanoscale 2011, 3, 4474.
(20) Sun, Z.; Luo, S.; Fan, L.-S. Transfer Mechanism of COS Reaction with CaO: Inert Marker Experiment and Density Functional Theory (DFT) Calculation. AIChE. J. 2011, 58, 2617.
(21) Sun, Z.; Yu, F.-C; Li, F.; Li, S.; Fan, L.-S. Experimental Study of HCl Capture Using CaO Sorbents: Activation, Deactivation, Reactivation, and Ionic Transfer Mechanism. Ind. Eng. Chem. Res. 2011, 50, 6034.
(22) Sun, Z.; Zhou, Q.; Fan, L.-S. Reactive Solid Surface Morphology Variation via Ionic Diffusion. Langmuir 2012, 28, 11827.
(23) Sun, Zhenchao, Qiang Zhou, and Liang-Shih Fan. "Formation of Core–Shell Structured Composite Microparticles via Cyclic Gas–Solid Reactions." Langmuir 29.40 (2013): 12520-2529. Print.